Appl Nanosci (2012) 2:385–388
DOI 10.1007/s13204-012-0112-x

ORIGINAL ARTICLE

First-principles study of naphthalene-based single-electron transistor

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Received: 26 November 2011 / Accepted: 30 March 2012 / Published online: 5 May 2012

Abstract We have performed first-principle calculations based on density functional theory (DFT) and non-equilibrium greens functions (NEGF) for calculating the charging energies of molecular system weakly coupled to an environment. We apply this approach to the molecule naphthalene, which is lying flat on gate dielectric between the source and drain electrodes. Our calculated values of charging energy for naphthalene in an isolated case are in good agreement with experimental values. Further, in an electrostatic environment, the result shows renormalization of molecular energy levels and therefore reduces the charging energy of naphthalene. Subsequently, the charge stability diagram of naphthalene based single-electron transistor (SET) has been obtained by calculating the charging energies as a function of an external gate potential. This diagram shows the dependence of SET conductance on the gate voltage and the source-drain bias. Our implementation is intended to predict the charging energies of the naphthalene-based SETs that reveals further scope in realization of the devices at nanoscale.

Keywords Single-electron transistor · Charging energy · Ionization energy · Electron affinity · Charge stability diagram

Introduction

Single-molecule single-electron transistor (SET) is a very interesting as well as an innovative device in nanoscience and nanoelectronics which has attracted the vast community of researchers. There have been a lot of discoveries dealing with experimental studies (Cuniberti et al. 2005; Liang et al. 2002; Kubatkin et al. 2003; Osorio et al. 2007; Yu et al. 2005; Thijssen and Van der Zant 2008), theoretical studies of single-molecule SETs (Stokbro 2010; Fatemi et al. 2011), are not widely reported. Recent experimental investigations on single-molecule SET constructing from bottom up approach, using organic molecule as an active component shows its applicability towards future nanoelectronic systems.

Theoretically, two limiting regimes can be distinguished, namely coherent transport (CT) for strong coupling between the molecule and the source/drain electrodes and coulomb blockade (CB) for weak coupling. The first-principle calculations for CT regime have been successfully performed by non-equilibrium green's function (NEGF) methods in conjunction with density functional theory (DFT) (Brandbyge et al. 2002; Xue et al. 2002; Rocha et al. 2005; Thgesen and Jacobsen 2005) or semi-empirical models (Magoga and Joachim 1997; Corbel et al. 1999; Cerda and Soria 2000; Emberly and Kirczenow 2000; Zahid et al. 2005; Kienle et al. 2006). However, in the case of single-molecule SET operating in CB regime, the transport is incoherent (Stokbro 2010). Therefore, another approach based on semi-empirical model for simulating the properties of single-molecule single-electron transistors (SETs) has been recently introduced (Kaasbjerg and Flensberg 2008) and showed the importance of including renormalization of molecular charge states due to the polarization of the environment.

Experiments on organic molecule have revealed that the addition energy, defined here as the difference between the molecular ionization potential (IP) and the electron affinity (EA), is strongly reduced from its corresponding gas phase

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value in single-molecule SETs (Kubatkin et al. 2003; Danilov et al. 2008; Osorio et al. 2007). Despite the great progress achieved, challenges are still present for the practical application of molecular electronics. The suitability of a standard DFT framework for electron transport in both the CB and CT regimes was also debated (Toher et al. 2005; Koentopp et al. 2008). Therefore, a more realistic and quantitative theoretical description is needed.

In this study, we have adopted the approach introduced (Stokbro 2010) and applied it to calculate the charging energy of a large molecule of naphthalene weakly coupled to an environment. Thus, we obtain the charge stability diagram of naphthalene-based SET by calculating the charging energies as the function of external gate potential. Specifically using first-principle approach, the influence of the SET environment on the positions of the molecular energy levels of naphthalene has been demonstrated.

Computational method

We have performed ab initio calculations for calculating the charging energies of naphthalene molecule in the gas phase and in electrostatic SET environment. For this purpose the total energies are evaluated by performing self-consistent calculations for different charge states of the molecule, i.e., with varying number of electrons on the molecule. The molecular IP and EA are given by the difference in total energy between the neutral and singly charged states of the molecule, i.e.,

$$\mathrm{IP} = E^{N-1} - E^{N} \text{ and } \mathrm{EA} = E^{N} - E^{N+1} \quad (1)$$

Here, N denotes the number of electrons in the neutral state of the molecule. The charged states with one electron added ($N + 1$) and removed ($N-1$) correspond to the anion and cation, respectively. The addition energy is given by the difference between IP and EA.

$$E_{\mathrm{add}} = \mathrm{IP} - \mathrm{EA} = E^{N-1} + E^{N+1} - 2E^{N} \quad (2)$$

All the calculations are carried out using DFT-based NEGF formalism which is implemented in Atomistix ToolKit (ATK 2011, quantumwise). The DFT model used here is based on pseudopotential with numerical localized basis functions. In this framework, a compensation charge is introduced for each atomic site. The compensation charge has the same charge as the pseudopotential and is used to screen the electrostatic interactions. We next extend the total energy functional to include interactions with a number of dielectric and metallic regions surrounding the system. Figure 1 illustrates a typical SET geometry, where naphthalene molecule is positioned on the top of a dielectric material and surrounded by metallic electrodes. Within the metallic regions the potential is fixed

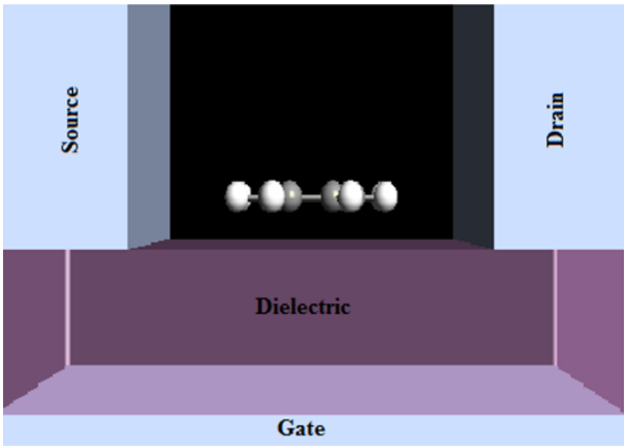

Fig. 1 A naphthalene molecule lying flat on the top of dielectric substrate between the source and drain electrodes with metallic back-gate resembling an electrostatic SET environment at zero gate and source-drain bias

to the applied bias on each respective electrode. For the calculations we use non-polarized DFT in the local density approximation (LDA) and expand the wave functions in double-zeta polarized (DZP) basis set. We apply Neumann boundary conditions, i.e., zero electric field. The system consists of a metallic back-gate, and above the gate there is 3.8 Å of dielectric material with dielectric constant 10 ε_0. The molecule is positioned 1.2 Å above the dielectric. To the left and the right of the molecule, there are metallic source-drain electrodes, respectively. Moreover, the distance between the molecule and the electrode is kept at 2.8 Å. We have taken the value of electrode work function as 5.28 eV which resembles the value of gold electrode (Riviere 1966).

Result and discussion

The DFT calculations have been performed in the gas phase and in the SET environment for naphthalene molecule. The gas phase values denoted as "isolated" in Table 1 are obtained from the total energies of the charged isolated molecule. While the "SET" values are obtained by

Table 1 The calculated and experimental values of ionization (I) and affinity (A) energies (all are in eV) for naphthalene in gas phase and in SET environment

Naphthalene	E_{I}^{+1} (eV)	E_{I} (eV)	E_{A} (eV)	E_{A}^{-1} (eV)
Experiment	–	8.14[a]	−0.191[a]	–
Isolated	13.19	7.72	−0.87	−6.07
SET	8.38	6.35	1.14	−0.69

[a] NIST server (http://cccbdb.nist.gov/) and Foerster et al. (2011)

calculating the total energies of the charged molecule in the electrostatic surrounding at zero gate and source-drain bias.

It is evident from Table 1 that for isolated case, our calculated values of charging energy for naphthalene are in good agreement with that of experimental values (Foerster et al. 2011). While in an electrostatic SET environment, the charging energy is strongly reduced as compared to its gas phase values. The reduction in the charging energy arises from the screening of the charged molecule by the surrounding dielectric and metal electrodes (Kaasbjerg and Flensberg 2008).

For naphthalene, we have compared our findings with the GW calculations (Neaton et al. 2006). They found the gas phase value for $E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} = 8.34$ eV and for naphthalene adsorbed on graphite, $E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} = 5.54$ eV, which is comparable with our values of $E_{\mathrm{I}} - E_{\mathrm{A}} = 8.59$ eV in the gas phase and of $E_{\mathrm{I}} - E_{\mathrm{A}} = 5.21$ eV in the electrostatic SET environment.

After that, we calculate the total energy of the different charge states in SET environment as a function of gate voltage (V_{G}) as shown in Fig. 2a. The total energy includes reservoir energy qW, where q represents charge of naphthalene molecule and W is the work function of gold electrode. Figure 2a shows that at zero gate voltage, the neutral molecule has the lowest energy and hence it is a stable charge state. Negative charge states lower energy by positive gate voltage, while positive charge states lower energy at negative gate potentials. This is in agreement with HOMO and LUMO levels following $-eV_{\mathrm{G}}$, thus, at positive gate voltage the LUMO level gets below the electrode Fermi level and therefore attracts an electron and the molecule gets negatively charged. At negative bias, the HOMO level gets above the electrode Fermi level, hence, an electron escapes from naphthalene and the molecule becomes positively charged.

The dependence of total energy on gate voltage can be understood by fitting a quadratic function to the data:

$$E = \alpha q V_{\mathrm{G}} + \beta (eV_{\mathrm{G}})^2 \tag{3}$$

Note that we assume the linear term to be proportional to the charge q on naphthalene, while the quadratic term arises from the polarization of the naphthalene and therefore is independent of q. By fitting the data we find for naphthalene, $\alpha = 0.6375$ eV and $\beta = -0.003$ eV^{-1}, where the variation with the charge state is ~ 0.01 eV for α and ~ 0.001 eV^{-1} for β. Thus, naphthalene is closely coupled with the gate. This is due to the fact that all atoms of naphthalene on an average are closer to dielectric substrate. Therefore, we observe almost linear relationship between total energy and gate voltage.

For a single-molecule SET operating in the coulomb blockade regime, charge transfer through molecule is possible when either the ionization potential (IP) or the electron affinity (EA) is positioned within the bias window. If on the other hand, no levels are present in the bias window, current is blocked and the molecule remains in a fixed charged state. To reach the regime where transport is possible, one can either shift the IP and EA levels with the gate voltage or apply a sufficiently large source-drain bias. The results are so-called charge stability diagram. We next calculate the charge stability diagram for naphthalene based SET as shown in Fig. 2b by evaluating total energies of the neutral, singly charged and doubly charged molecule as a function of gate and source-drain bias. The different colors in this diagram show the number of molecular levels inside the bias window for given values of the gate and source-drain bias. Charge stability diagram for naphthalene based SETs therefore provide a useful tool for measuring

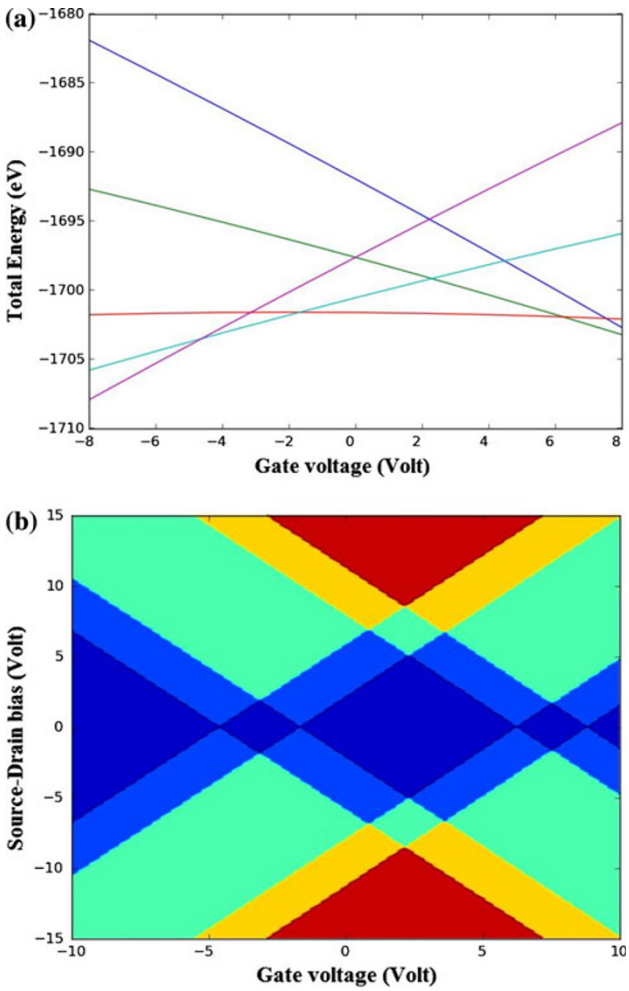

Fig. 2 **a** The total energy as a function of gate voltage for naphthalene in the SET environment. Different curves for different charge states of naphthalene, *blue* (−2), *green* (−1), *red* (0), *turquoise* (1), *violet* (2); **b** Charge stability diagram for naphthalene based SET. The *color* shows the number of charge states *dark blue* (−2), *blue* (−1), *red* (0), *green* (1), *yellow* (2) within the bias window for a given gate voltage and source-drain bias

the energy differences between the molecular levels. The conductance is directly related to the number of energy levels inside the bias window and hence this diagram indicates an indirect measure of the current level for a given gate and source-drain voltage. We observe that the excitation energy of naphthalene-based SET for second electron is much smaller than that of first electron. It can also be noted that charge stability diagram depends only on the difference in energies between charge states and second-order term in Eq (3) is independent of charge states and hence in charge stability diagram, the non-linear dependence of the total energy on gate voltage is not observed.

Conclusion

We performed an ab initio calculation to obtain the charge stability diagram of naphthalene based SET by calculating the charging energies as a function of external gate potential. The present study reveals that for isolated case, the charging energies of naphthalene are in good agreement with that of experimental values. Further, it is also observed that the SET environment renormalizes the molecular energy levels and hence reduces the charging energies for the naphthalene molecule. The present investigation further demonstrates the use of ab initio method to gain new insights into the properties of single-molecule SET operating in coulomb blockade regime.

Acknowledgments The authors are thankful to the Computational Nanoscience and Technology Lab (CNTL), ABV Indian Institute of Information Technology and Management, Gwalior (India) for providing computational facilities.

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